# Vapor Pressure of Water over Plutonium Dioxide


PI: D. Kirk Veirs

Experimental Contributors: Dane Spearing, John S. Morris, Max Martinez

Intellectual Contributors: Mark Paffett, Roland Schulze, Eddie Moody, John Lyman

Nuclear Materials Technology Division
Chemical Sciences and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545

# Scope

To measure the heat of adsorption of water on plutonium oxide and materials such as $CaCl_2$ and $MgCl_2$ containing up to 30 wt% of $PuO_2$.  Develop a model to predict the vapor pressure of water over these materials at temperatures up to 250 C.  Experimentally verify the predictive capability of the model.

Customers:  All sites planning to send plutonium oxide materials to long-term storage.

# Cost and Schedule

Costs to date: $92k 47%

Schedule:

| Activity | Progress (%) |
|---|---|
| $PuO_2$ measurements | 75% |
| $CaCl_2$ measurements | 25% |
| $MgCl_2$ measurements | 0% |
| Mixtures | 0% |

# Approach

Experiments

Pressure/temperature experiments with $PuO_2$ powders exposed to varying amounts of water.

Modeling

Use the well known vapor pressure of water and literature values of the heat of adsorption of water onto plutonium oxide to calculate the vapor pressure as a function of temperature and compare to experiments.

# Background

- 3013 Storage Standard "Stabilization, Packaging, and Storage of Plutonium-Bearing Materials" allows 0.5 wt.% $H_2O$. The original concern was limiting the amount of $H_2$ gas generation to less than 700 psi.
- Thermal modeling of a 3013 inner can within a 3013 outer can placed within a 9975 transportation container that is placed in the sun on asphalt on a hot day indicates internal temperatures up to 250 C.
- Available volume of 3013 inner container with 5kg $PuO_2$ is 2100 $cm^3$. Therefore a vapor density of 25 g/2100 $cm^3$ = 0.012 g/$cm^3$ could be attained corresponding to a saturated vapor pressure of 345 psia at 221 C.
- In the presence of chloride salts, this may result in accelerated corrosion.
- Methods to detect pressure rise due to $H_2$ gas generation may result in false positives due to water vapor pressure.

# Moisture uptake by $PuO_2$

Moisture uptake by $PuO_2$ powders depends upon:

relative humidity

specific surface area

Specific surface area

- Plutonium dioxide SSA can vary from 50 to 0.1 $m^2/g$.
- 1 monolayer of water is 0.20 $mg/m^2$ or from 1.0% to 0.002%.
- 0.5wt.% of water can vary from 0.5 to 250 monolayers.
- Typical calcined plutonium oxide has an SSA between 5 and .5 $m^2/g$ or 5 to 50 monolayers.

Relative Humidity

PuO2 powders can adsorb over 0.5 wt% at relative humidities of less 70%.

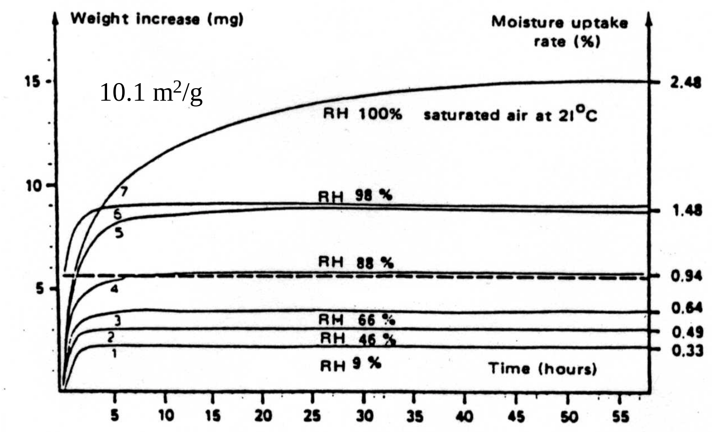


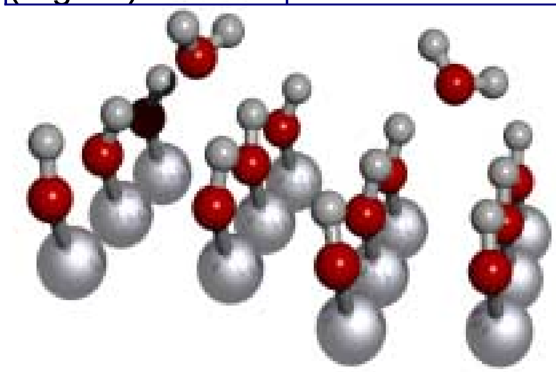

Figure 3. Moisture uptake by $PuO_2$ powder dried at 600°C.

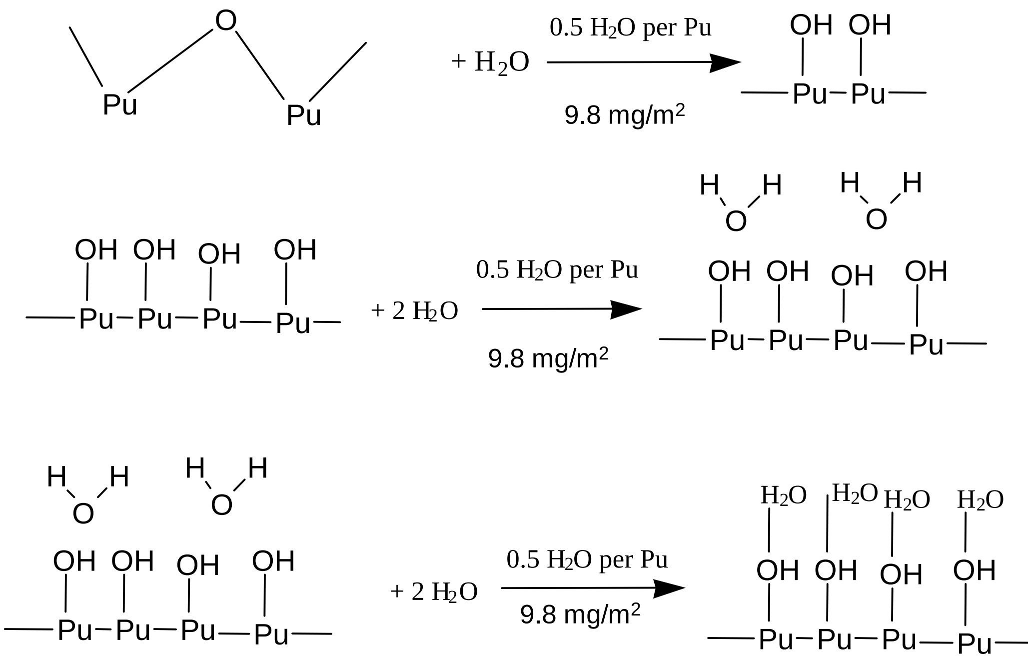
A. Bohhamou and J. P. Beraud, Analusis **8**, 376 (1980)

# Water Adsorption from a Crystallographic Point of View

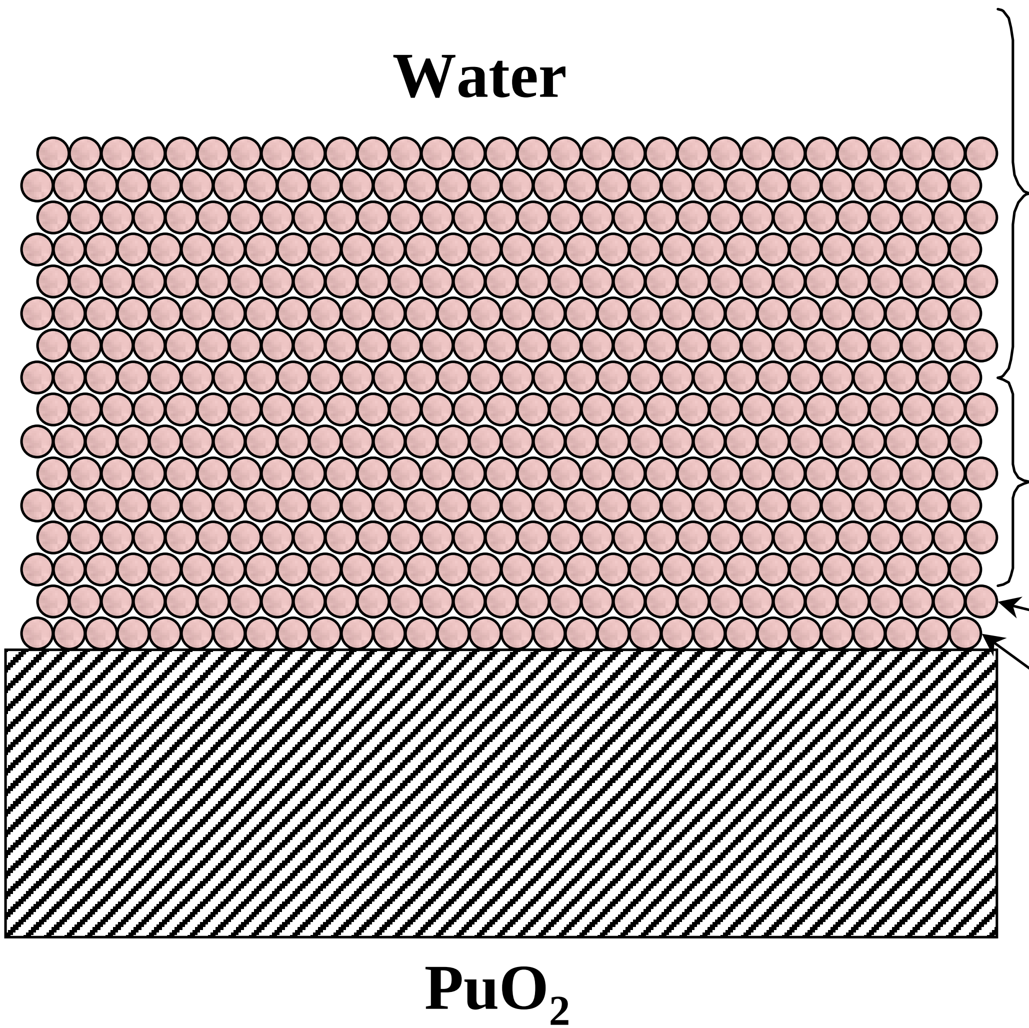
$PuO_2$ can be described by three dominant faces (100,110,111)

| | 100 face | 110 face | 111 face |
|---|---|---|---|
| Pu Atom Density (atom/Å$^2$) | 0.0687 | 0.0486 | .0793 |
| Sorbed Water (mg/m$^2$) | 0.205 | 0.145 | 0.237 |
| Stakebake (average mg/m$^2$) | 0.24 | | |
| Haschke (mg/m$^2$) | 0.22 | | |
| Water (mg/m$^2$) | 0.28 | | |





# Initial $PuO_2$/water model




All other layers $\Delta H_{vap}$ = 44 kJ/mol
the heat of vaporization of water.

Layers 3-8 $\Delta H_{ads}$ = 63 kJ/mol
Haschke 1997 distinguishes layers;
choose midpoint between water and
2nd layer for $\Delta H_{ads.}$

2nd layer $\Delta H_{ads}$ = 84 kJ/mol
Stakebake 1973

1st layer $\Delta H_{ads}$ = 172 kJ/mol
Stakebake 1973/Paffett 1999

# Model of the pressure of water over $PuO_2$

- Assume 0.5 wt% $H_20$ adsorbed on oxide (DOE 3013 Standard)

- Assume 0.22 mg of $H_20/m^2$ (Haschke, Ricketts 1997)

- Assume $\Delta H_{vap}$ of 285 kJ/mol for the first monolayer, 84 kJ/mol for second monolayer, 63 kJ/mol for the next six monolayers, and 42 kJ.mol (that for water at room temperature) for all remaining layers.

- Gas pressure calculated to first virial coefficient accuracy.

- Use Clausius-Clapeyron equation: $$P = c \cdot e^{\frac{-\Delta H_{vap}}{RT}}$$

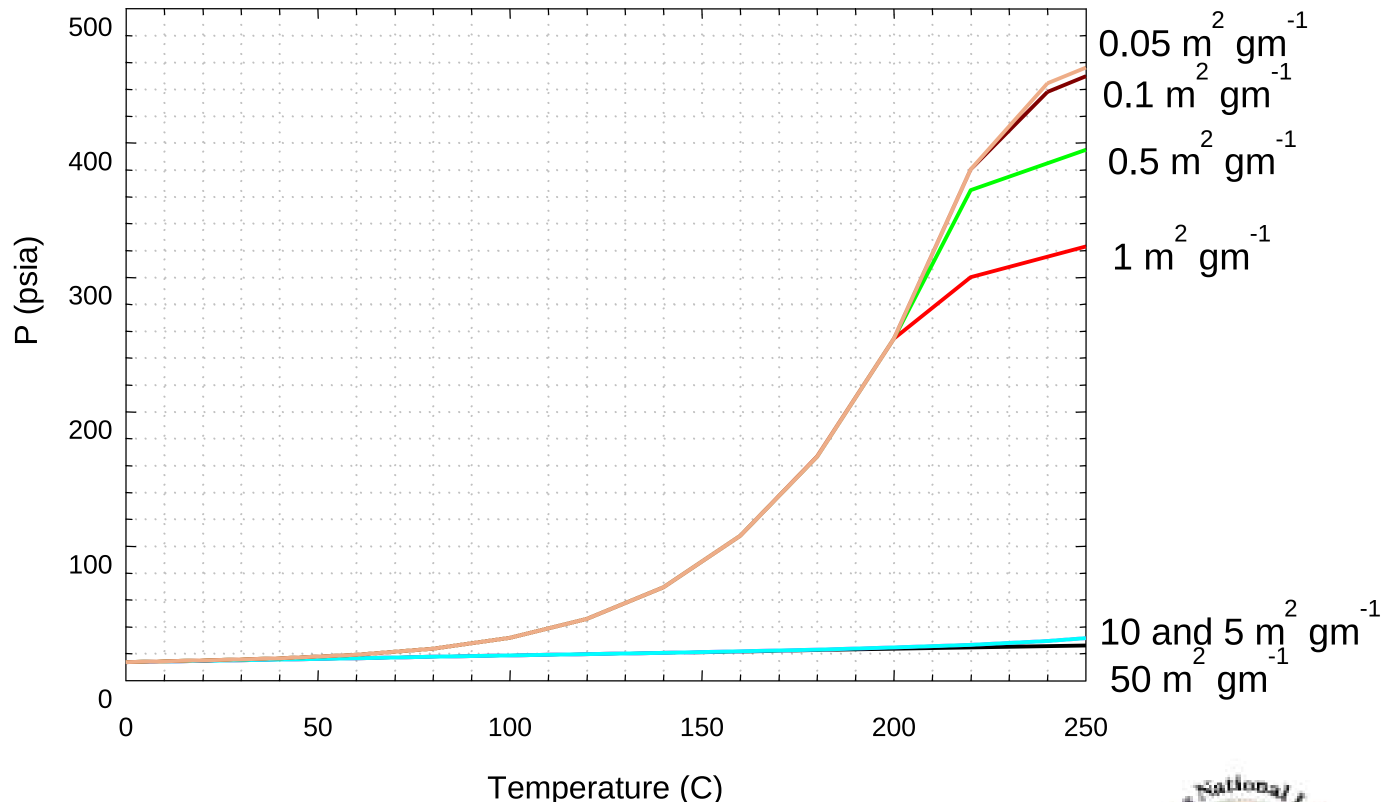
- c calculated from the vapor pressure of pure water.

- Vary specific surface area.

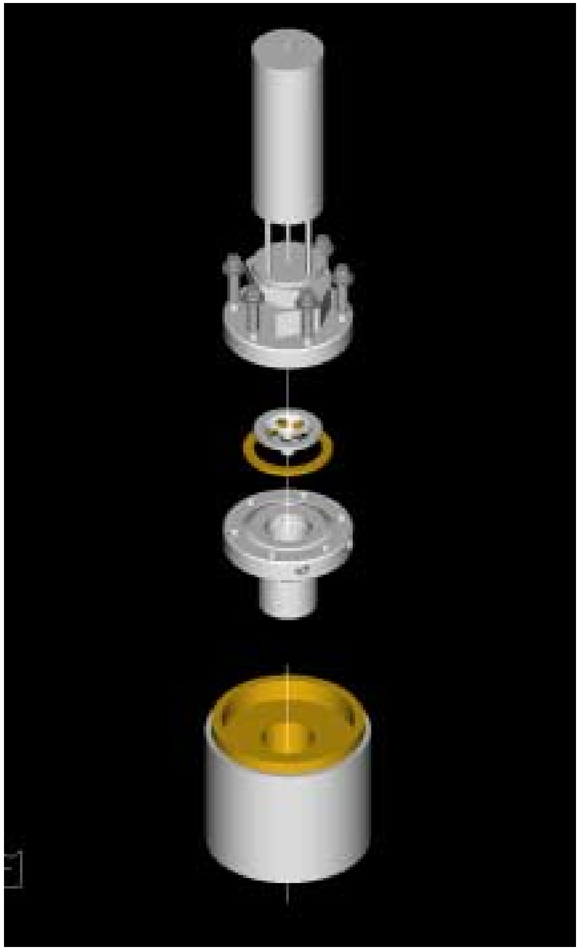
# Surface Area Dependence

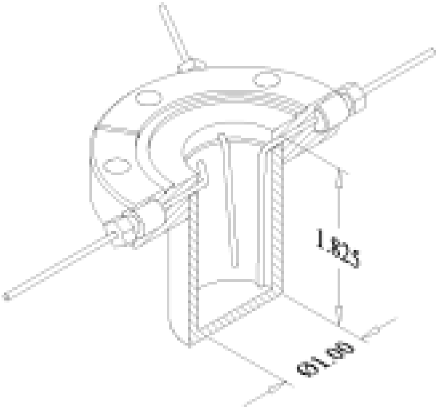
| | | | | | | |
|---|---|---|---|---|---|---|
| | Number of monolayers for different specific surface area oxides assuming a 0.22 grams of $H_20$ per square centimeter. Five kilograms of PuO2 with 0.5 wt% water. | | | | | |
| | | | | | | |
| SSA | monlayer | | | | | |
| ($m^2$ $gm^{-1}$) | layer 1 | layer 2 | layers 3-8 | layers 9- | | |
| 50 | 0.5 | 0 | 0 | 0 | | |
| 10 | 1 | 1 | 0.3 | 0 | | |
| 5 | 1 | 1 | 2.5 | 0 | | |
| 1 | 1 | 1 | 6 | 15 | | |
| 0.5 | 1 | 1 | 6 | 37 | | |
| 0.1 | 1 | 1 | 6 | 219 | | |
| 0.05 | 1 | 1 | 6 | 446 | | |
| | | | | | | P at 250 C |
| Percentage of water in each layer class | | | | | | (psia) |
| 50 | 100% | 0% | 0% | 0% | | 27 |
| 10 | 43% | 43% | 13% | 0% | | 33 |
| 5 | 22% | 22% | 56% | 0% | | 33 |
| 1 | 4% | 4% | 26% | 65% | | 330 |
| 0.5 | 2% | 2% | 13% | 82% | | 405 |
| 0.1 | 0% | 0% | 3% | 96% | | 461 |
| 0.05 | 0% | 0% | 1% | 98% | | 468 |
| | | | | | | |

# Pressure vs. Temperature as a Function of Surface Area



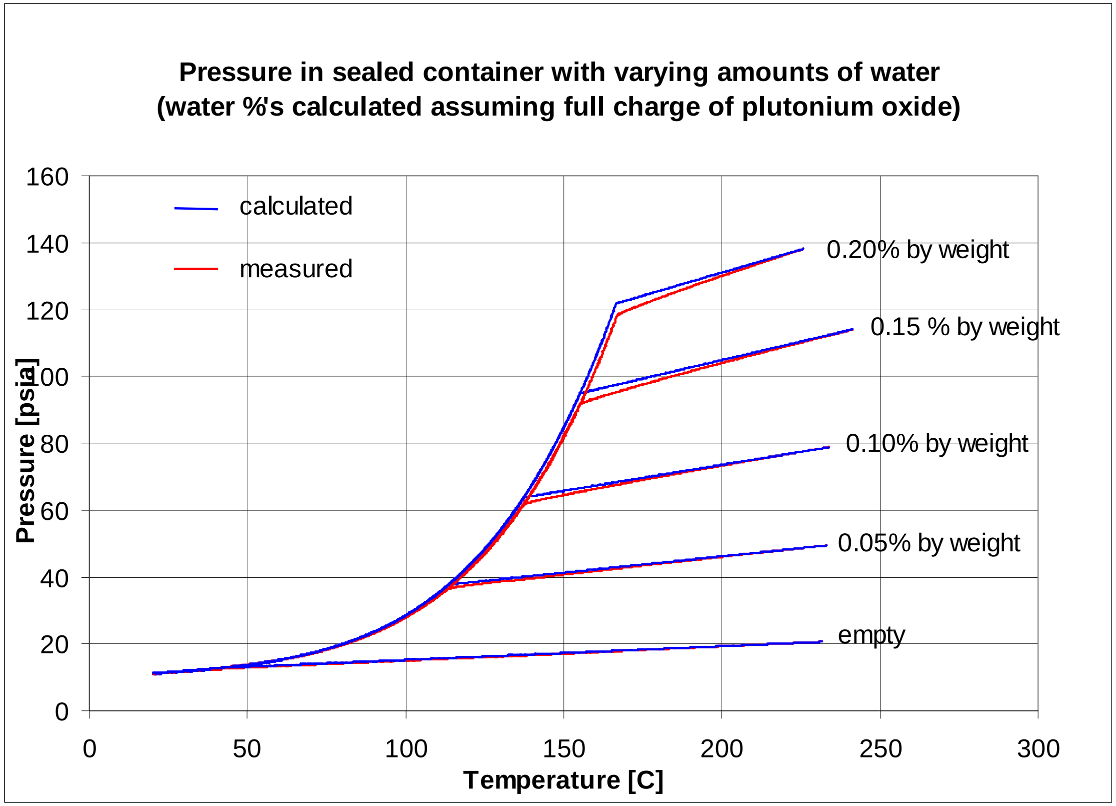
# Experimental





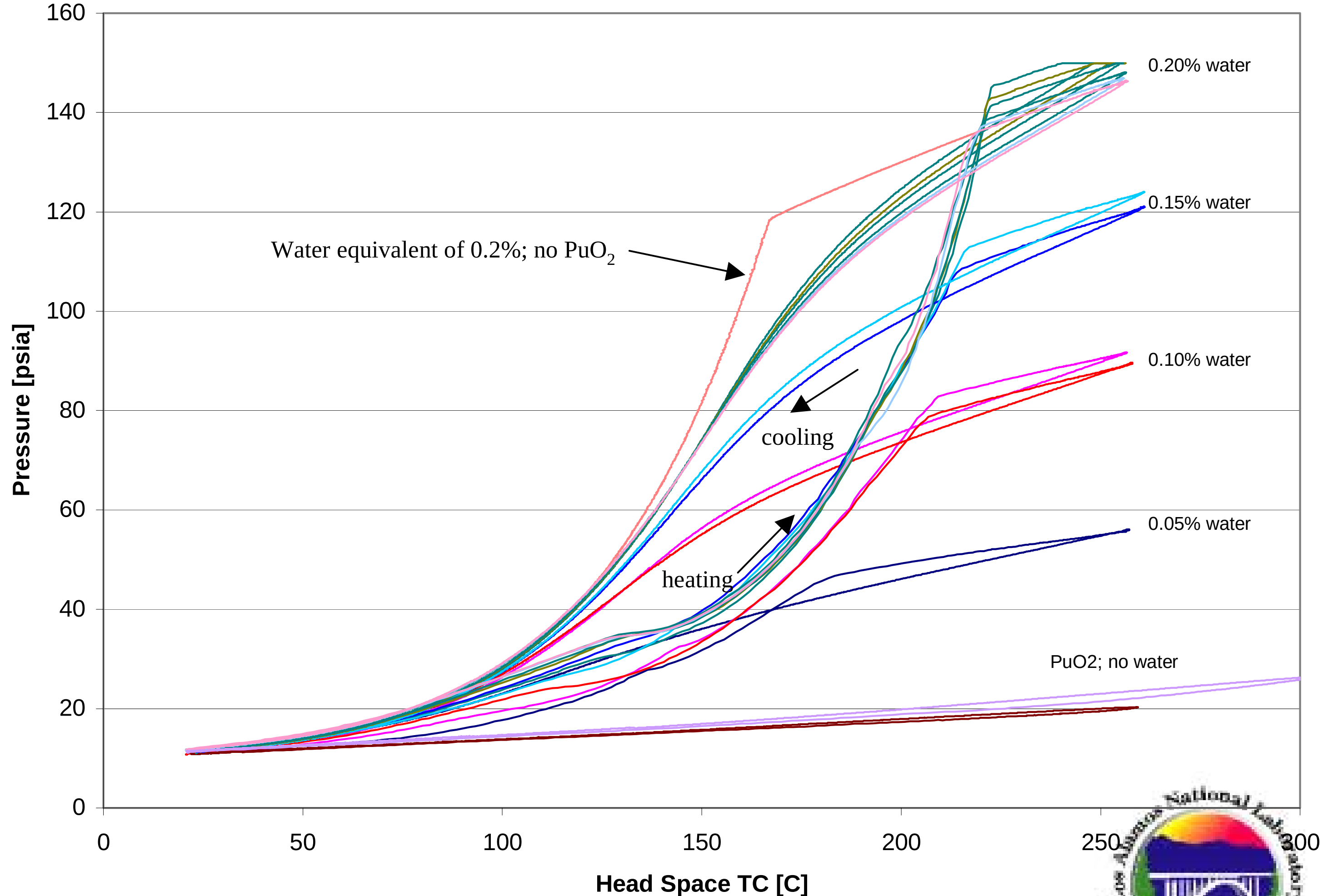

- Pressure sensor rated to 150 psia and 300 C.
- Volume of 26 cm$^3$ - 1% of 3013 container.
- Heated in copper block; 0.5” insulation.
- Three thermocouples - in head space gas, in oxide next to container wall, equidistance between bottom and walls.

# First test of apparatus and model is with water alone.

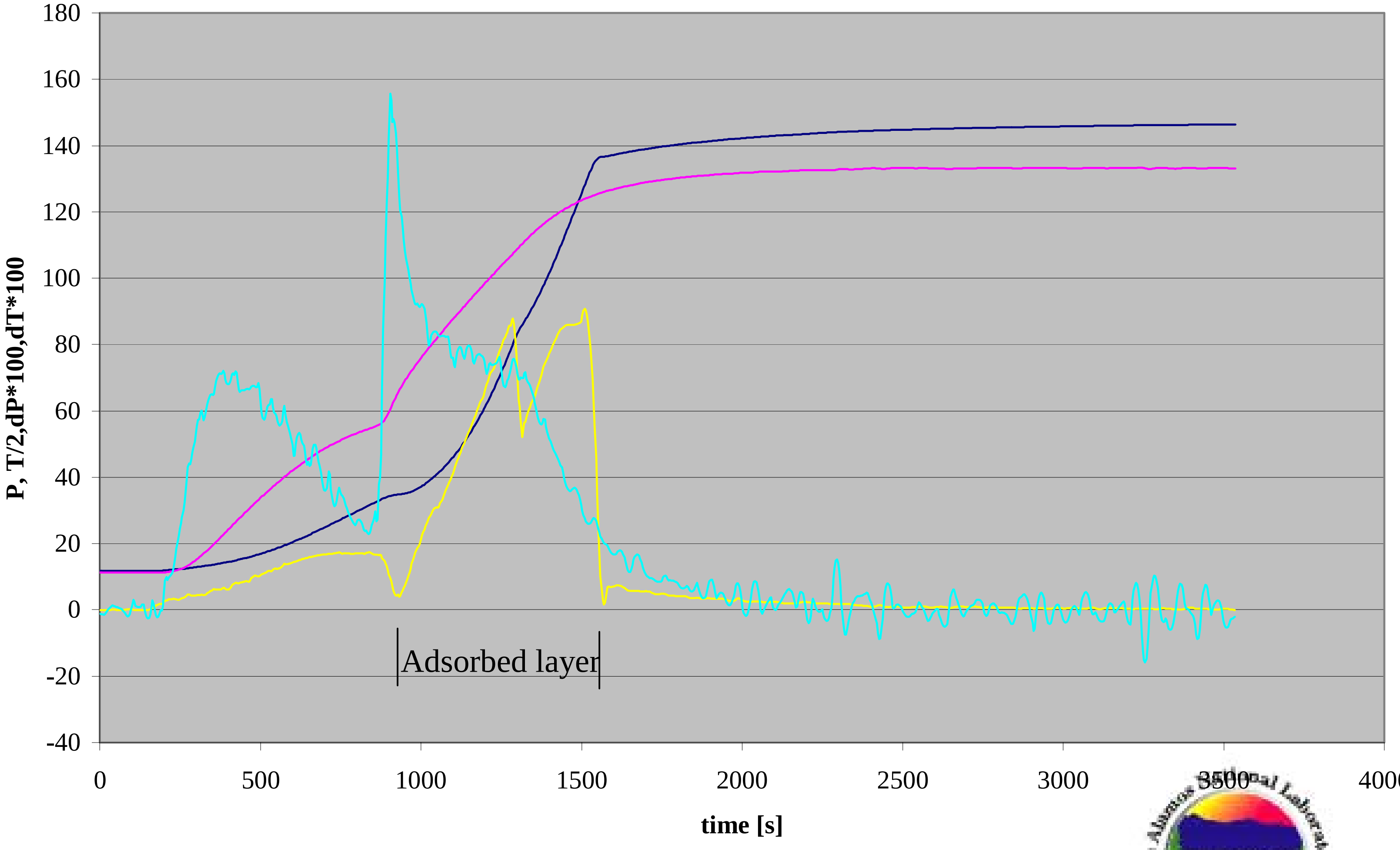



•Experimental measurements with water (no $PuO_2$) in sealed container agree very well with model.

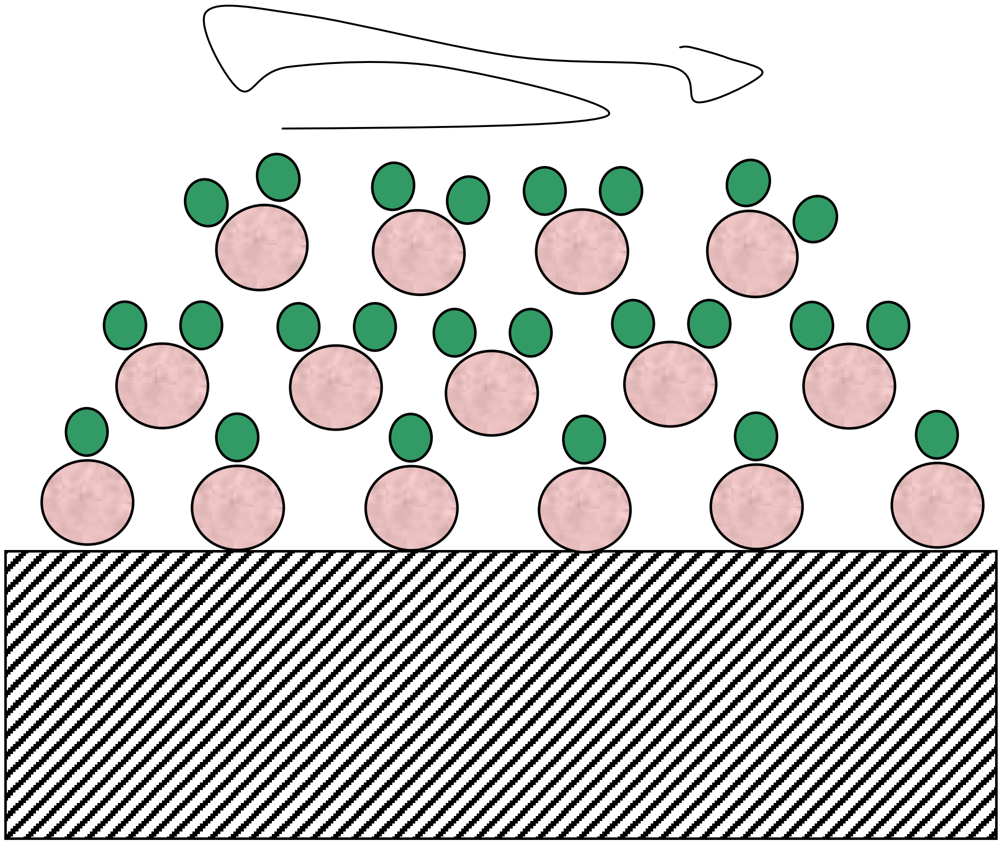
# Measured vapor pressure of water exposed to $PuO_2$



# ARF-114 run 14



# Current $PuO_2$/water model



**$PuO_2$**

Multilayers of water
$\Delta H \approx 44$ kJ/mol

Layer 3: Second molecularly adsorbed monolayer
$\Delta H \approx 44$ kJ/mol or 47 kJ/mol

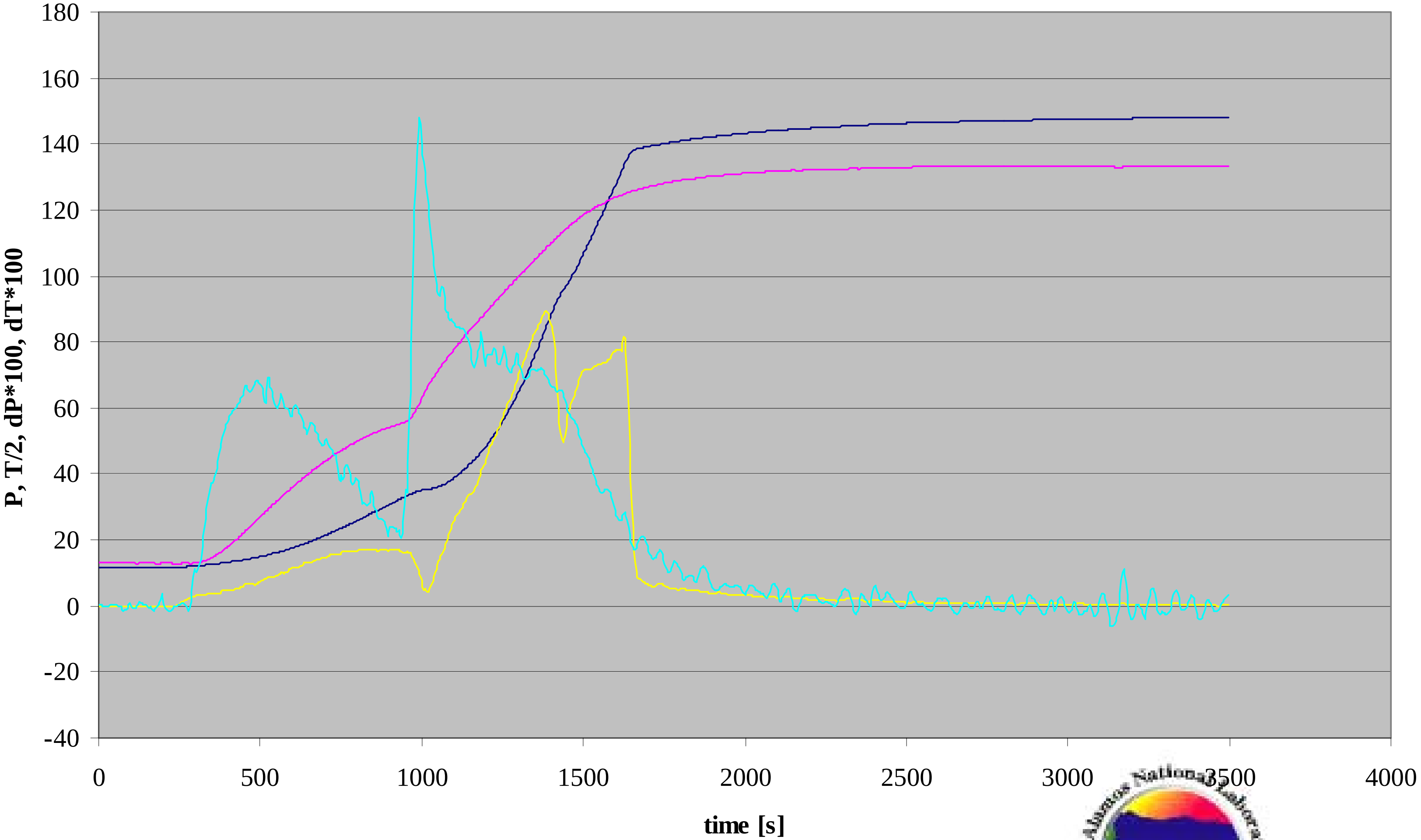
Layer 2: First molecularly adsorbed monolayer
$\Delta H \approx 47$ kJ/mol or 80 kJ/mol

Layer 1: Hydroxyl layer equivalent to 1/2 monolayer
$\Delta H \approx 170$ kJ/mol

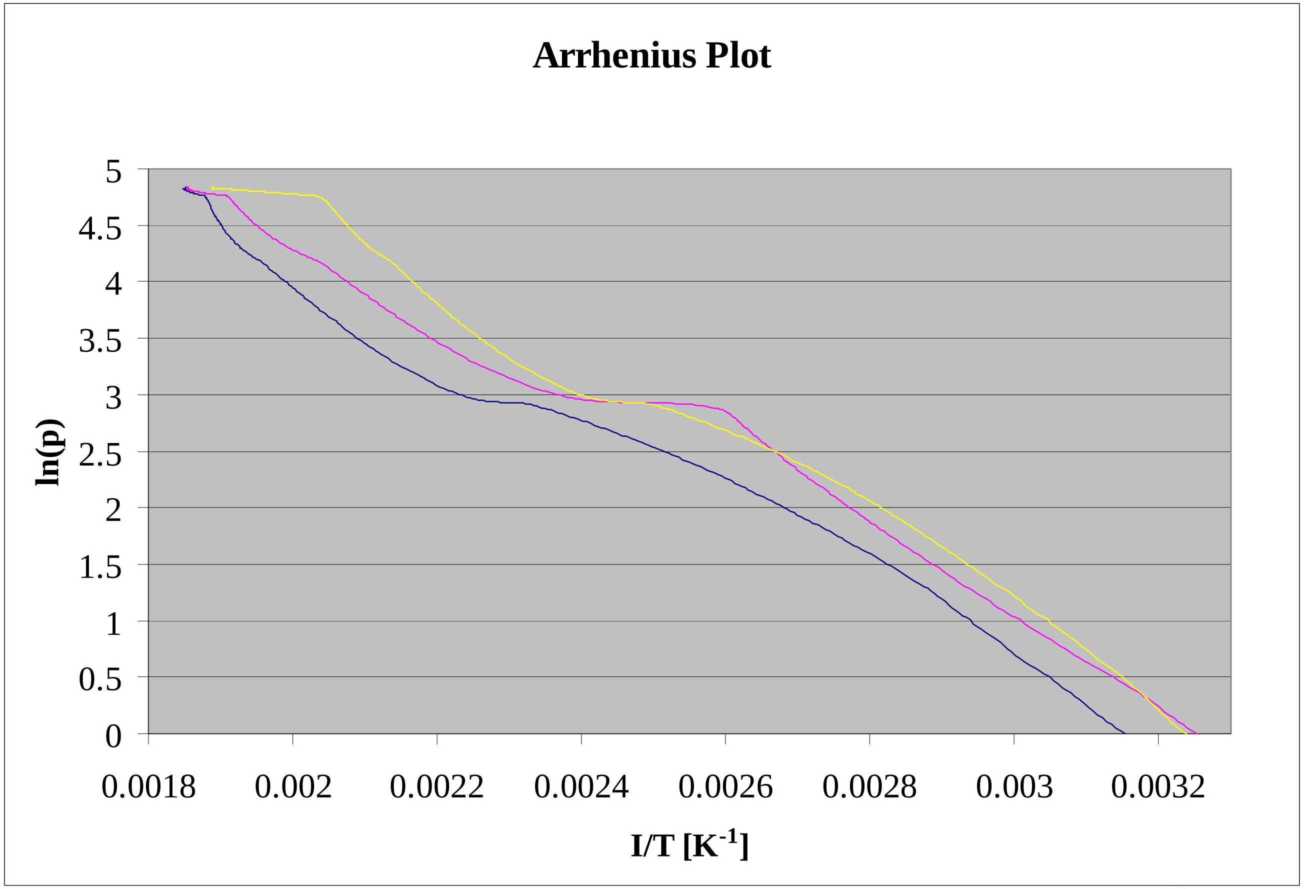
# Conclusions

•The vapor pressure of water adsorbed onto plutonium dioxide will be the same as the vapor pressure of water at the specified temperature for all layers of water excluding the first molecularly adsorbed layer.
•The vapor pressure of water arising from the first molecularly adsorbed layer will be less than the vapor pressure of water at the specified temperature by a relatively small amount; 30 psia maximum difference was observed in these experiments.
•The specific surface area of the plutonium dioxide powder and the amount of adsorbed water determines the vapor pressure as a function of temperature.

# ARF-114 run 12



# Regions in heating curve can be used to obtain $\Delta H_{ads}$



# $\Delta H_{ads}$ for observed monolayer

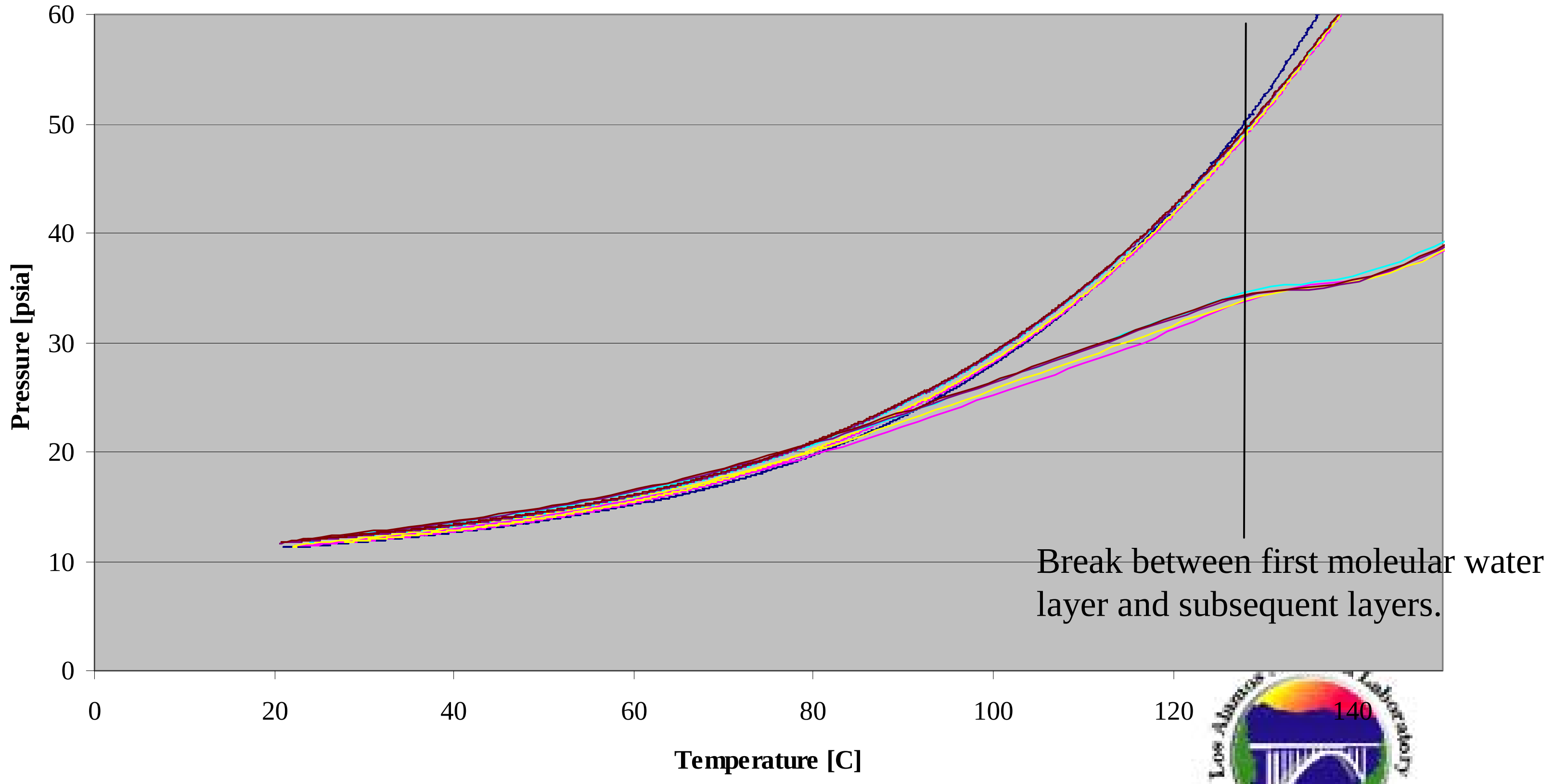
Determined from five runs in this experiment
kJ/mol

| | 009 $\Delta H$ | 010 $\Delta H$ | 012 $\Delta H$ | 013 $\Delta H$ | 014 $\Delta H$ | Average $\Delta H$ | sigma | |
|---|---|---|---|---|---|---|---|---|
| TC1 | 41.6 | 39.2 | 41.2 | 38.1 | 38.7 | 39.8 | 1.6 | Water region |
| TC2 | 35.6 | 33.5 | 35.5 | 32.5 | 33.4 | 34.1 | 1.4 | water is 42.9 at 50 C |
| TC3 | 45.2 | 42.8 | 45.5 | 42.9 | 43.7 | 44.0 | 1.3 | |
| TC1 | 40.4 | 40.6 | 40.3 | 40.5 | 41.8 | 40.7 | 0.6 | monolayer region |
| TC2 | 34.6 | 35.3 | 35.0 | 35.3 | 35.8 | 35.2 | 0.4 | water is 36.3 at 175 C |
| TC3 | 43.9 | 43.9 | 43.7 | 43.5 | 44.6 | 43.9 | 0.4 | |

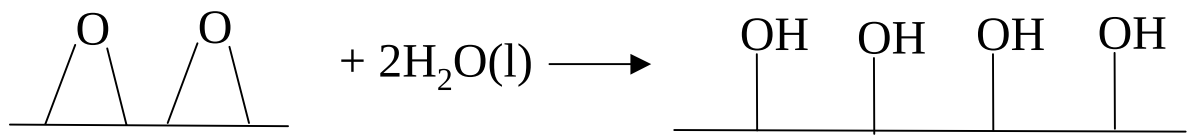
$\Delta H_{ads}$ for first molecularly adsorbed monolayer is reported as 84 kJ/mol by Stakebake 1973.

# Water layers beyond first behave like water.

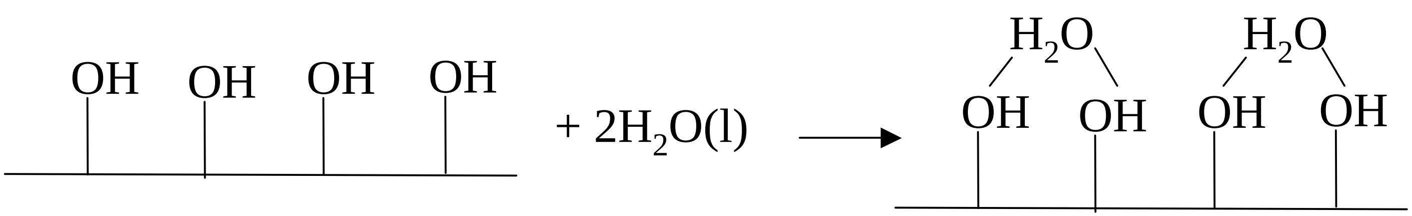
**P vs T for 0.2 wt. % water.**
**Detail of the layer preceding the first molecularly adsorbed layer.**
**Pressure as a function of temperature is the same as pure water.**



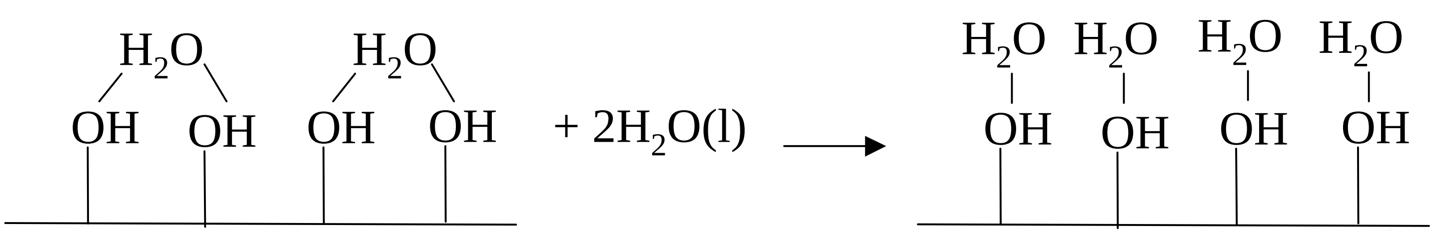
# Model of Water on Thorium Oxide from Literature




$(\Delta H_a = -19\ \text{kcal/mol})$




$(\Delta H_a = -8.5\ \text{kcal/mol})$




$(\Delta H_a = -1\ \text{kcal/mol})$

Heat of Immersion in the Thorium Oxide-Water System. IV. Variation of the Net Differential Heat of Adsorption with Specific Surface Area by H. F. Holmes, E. L. Fuller, Jr., and C. H. Secoy, The Journal of Physical Chemistry **72**, 2095 (1968).